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# Synthesis and Properties of Low-Bandgap Zwitterionic and Planar Conjugated Pyrrole-Derived Polymeric Sensors. Reversible Optical Absorption Maxima from the UV to the Near-IR

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Described are the polymerizations of three new dibrominated carbonyl-stabilized ylide monomers using copper-bronze in DME to afford polymers that are soluble in common solvents and have unique optical and electronic properties. The first monomer is a zwitterionic $N$-(butyl)pyrrolinium oxide derivative which, upon polymerization, gives a polymer that has a strong optical absorbance at 520 nm in $CCl_4$. An inter-unit ionic interaction is proposed to explain this large red-shifted band. Brønsted bases and Lewis bases induce a reversible structural change in the polymer to give bathochromic shifts from the visible to the near-IR spectral region. Upon mild reduction of the zwitterionic polymer with Pd/C and $H_2$ (1 atm), some of the extended conjugation is lost, but a polymer forms that has an enormous optical absorption maximum range from the near-UV (290 nm) to the near-IR (886 nm) depending on the solvent or hydroxide concentration. A sample of the reduced polymer can be dispersed in platicized poly(vinyl chloride). The flexible polymer composite reversibly changes from dark blue-brown in aqueous sodium hydroxide to bright yellow-orange in aqueous HCl. The second monomer, a zwitterionic $N$-(dodecyl)pyrrolinium oxide derivative, was also synthesized in three steps from pyrrole, and upon polymerization, gives rise to a polymer which also responds reversibly towards Brønsted and Lewis bases. This polymer can be solution cast into flexible-free standing films. The thi

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# Synthesis and Properties of Low-Bandgap Zwitterionic and Planar Conjugated Pyrrole-Derived Polymeric Sensors. Reversible Optical Absorption Maxima from the UV to the Near-IR

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## Abstract

Described are the polymerizations of three new dibrominated carbonyl-stabilized ylide monomers using copper-bronze in DME to afford polymers that are soluble in common solvents and have unique optical and electronic properties. The first monomer is a zwitterionic $N$-(butyl)pyrrolinium oxide derivative which, upon polymerization, gives a polymer that has a strong optical absorbance at 520 nm in $CCl_4$. An inter-unit ionic interaction is proposed to explain this large red-shifted band. Brønsted bases and Lewis bases induce a reversible structural change in the polymer to give bathochromic shifts from the visible to the near-IR spectral region. Upon mild reduction of the zwitterionic polymer with Pd/C and $H_2$ (1 atm), some of the extended conjugation is lost, but a polymer forms that has an enormous optical absorption maximum range from the near-UV (290 nm) to the near-IR (886 nm) depending on the solvent or hydroxide concentration. A sample of the reduced polymer can be dispersed in platicized poly(vinyl chloride). The flexible polymer composite reversibly changes from dark blue-brown in aqueous sodium hydroxide to bright yellow-orange in aqueous HCl. The second monomer, a zwitterionic $N$-(dodecyl)pyrrolinium oxide derivative, was also synthesized in three steps from pyrrole, and upon polymerization, gives rise to a polymer which also responds reversibly towards Brønsted and Lewis bases. This polymer can be solution cast into flexible-free standing films. The third monomer is a zwitterionic $N$-(oligoethylene glycol monomethyl ether)pyrrolinium oxide derivative

which, upon polymerization, affords a polymer which not only responds reversibly towards Brønsted and Lewis bases, but it is also water soluble and optically sensitive toward the addition of specific salts. The presence of the oligoethylene substituents is critical for the dramatic ionochromic response. Additionally, Pd-catalyzed cross coupling methodology can be used for the incorporation of the $N$-(butyl)pyrrolinium oxide monomer unit into an AB-type oligomeric system where the B component is a 1,4-phenylene moiety.

In an effort to maximize the extended $\pi$-conjugation in polymers and to study their corresponding electronic and optical properties, several have undertaken the synthesis of new conjugated organic polymers that have a planar or near-planar conformation between the consecutive repeat units.[1,2] We detail here the syntheses of three unique zwitterionic pyrrole-derived monomers which, upon polymerization, give polymeric materials that can reversibly convert to a linear and planar conjugated polymer with a solution bandgap of approximately 1.1 eV. The materials possess a reversible and enormous pH, solvent, or ion dependent absorption spectral range from the UV to the near-IR spectral region. Soluble polymeric materials that can respond dramatically and reversibly to external stimuli could have importance in the development of organic-based optical and electronic sensors,[2] while polymers with absorptions in the near-IR can serve as dyes for optical data discs.[3]

The synthesis of the new pyrrole-derived zwitterionic polymer began with the *N*-alkylation of pyrrole using 1-*n*-bromobutane under standard phase transfer conditions to afford **1**.[4a] Bromination[5] of **1** using 2 equivalents of NBS gave the dibrominated pyrrole derivative **2**. Our initial report for the oxidation of **2** involved heating **2** in a solution of 70% nitric acid and 20% fuming sulfuric acid to afford the resonance stabilized azomethine ylide pyrrolinium oxide **3**.[6] We report here that simply the use of 70% nitric acid at 0°C can affect the same transformation in a similar yield (eq 1). Note that two resonance forms exist for **3**, therefore, there were only six
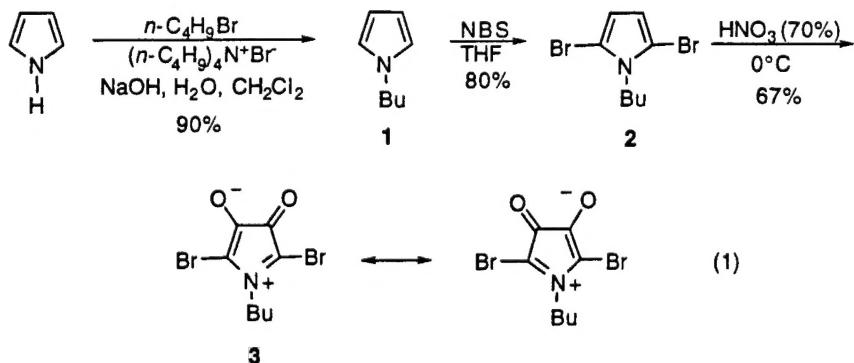
peaks in the $^{13}C$ NMR spectrum and there was no hydroxyl absorbance in the FTIR spectrum. In addition to $^1H$ NMR and elemental analysis confirmation of the structure, substantiation of the zwitterionic pyrrole nature was obtained by reduction of **3** to afford the enol **4** (eq 2).[7] The $^{13}C$
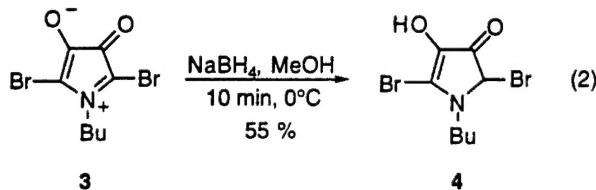


NMR (8 resonances) and FTIR (1697 cm$^{-1}$ for the conjugated carbonyl and 1617 cm$^{-1}$ for the alkene) are consistent with the enol form as shown. A resonance at $\delta$ 5.26 (br s, 2 H) in the $^1H$ NMR suggests that the keto-enol tautomerism is rapid on the NMR time scale. On standing in air, **4** slowly oxidized back to **3**. Furthermore, as is common to azomethine ylides, **3** underwent a cycloaddition reaction with cyclopentadiene to afford the single adduct, **5** or **6**, in quantitative yield (eq 3). NOESY NMR experiments were inconclusive for ascertaining the stereochemistry of the
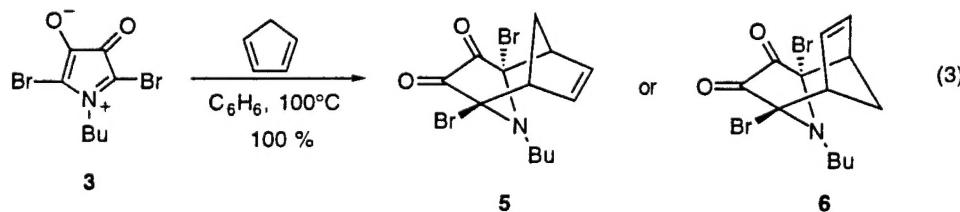


adduct, and since the assignment was not critical for further studies, we did not attempt a crystallographic determination of the relative stereochemistry.

We then sought to polymerize **3** using a variety of coupling methods.[8] Although (COD)$_2$Ni(0)[9] did induce coupling, the degree of polymerization ($M_n = 580$) was very low. Attempted formation of the mono-Grignard reagent,[5] for transition metal-catalyzed coupling, caused decomposition of the monomer. Copper(II) triflate[10] and Rieke copper[11] also failed to afford any polymeric product. Classical Ullmann[12] coupling using copper-bronze (Aldrich) also failed when utilizing the common solvents (DMF, quinoline, tetramethylurea, or pyridine);

however, in DME, copper-bronze-promoted polymerization (200°C, screw cap tube) of **3** afforded the desired polymer **7** (eq 4) in 56% yield after fractional precipitation (CH$_2$Cl$_2$, CH$_3$OH). The
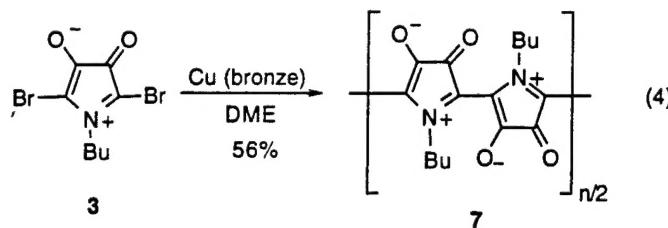


precipitation dramatically sharpened the polydispersity (PD) to 1.15-1.25 with $M_n$ = 3,910 (size exclusion chromatography, polystyrene standards).[13] If the reaction was run for 40 h, the molecular weight peaked at $M_n$ = 4,980, with PD = 1.54. Continued heating caused no increase in the molecular weight. No detectable bromide content was observed since the excess Cu(0) carries out oxidative additions on nearly all aryl bromide locations with subsequent end group protonations on workup; a commonly observed feature of Ullmann reactions.[12b,c] A macrocyclic structure cannot be ruled out, however, to have a pyrrole ring system with all the nitrogen atoms pointing inward would require 10 pyrrole units to complete the ring.[8c] A macrocycle with all the oxygen atoms pointing inward would require far more pyrrole units, therefore excluding a monomeric Cu-template driven macrocyclization.

We were able to substitute the bromides on **3** with iodides using sodium iodide.[14] Polymerization of the iodide substituted monomer **8** had little affect on the degree of polymerization or PD; however, the yield increased from 56% to 67% (eq 5).
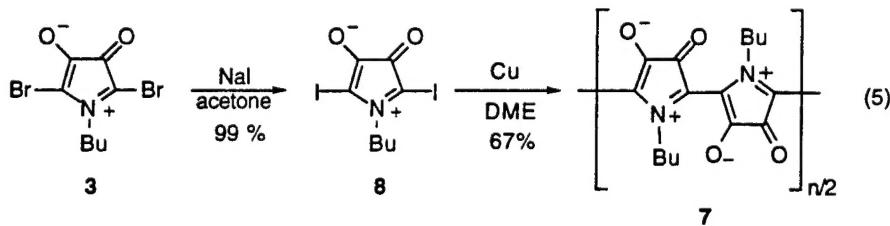


**7** is an intrinsic semiconductor exhibiting an undoped conductivity of 1.4 x 10$^{-5}$ Ω$^{-1}$ cm$^{-1}$ and an iodine doped conductivity of 4.2 x 10$^{-4}$ Ω$^{-1}$ cm$^{-1}$ (4-point probe, pellet). The low doped

conductivity of the system may be due to the presence of the carbonyl functionality which can retard polaronic or bipolaronic migrations.[1j] The material was tested for photoconductivity; however, preliminary results indicated no change in the resistivity upon polymer photo-illumination. Thermogravimetric analysis (TGA, 10°C/min, $N_2$) on **7** showed a 10% weight loss at 318°C and with a rapid weight decrease at 400°C.

The optical spectra for **7** were most interesting. Polypyrrole has an absorption maximum of 420 nm (solid), but it is intractable. *N*-alkylated polypyrrole is soluble, however, the increased steric repulsions between the consecutive aryl units causes a hypsochromic shift to approximately 380 nm.[8] The absorption maximum of **7** (Figure 1) exhibits a strong bathochromically shifted
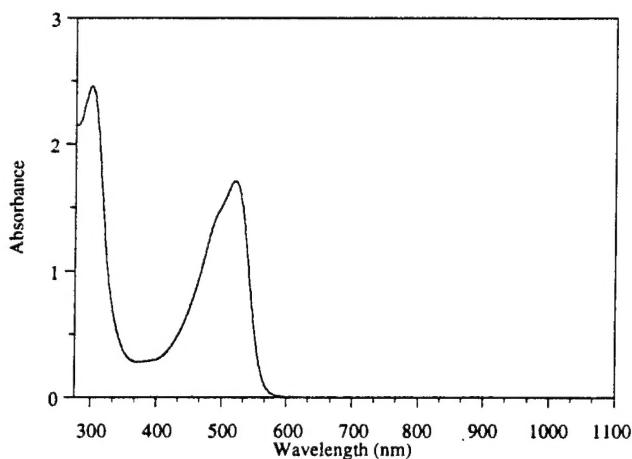


**Figure 1.** Spectrum of **7** in $CCl_4$.

absorption that may be due to ionic interactions that force a diminution in the inter-unit twist angle.[2] Solvatochromic effects are also consistent with the structural assignment in that the following trend of $S_0$-$S_1$ ($\pi-\pi^*$) absorption maxima are present for **7**: $CCl_4$, 520 nm (Figure 1); THF, 512 nm; EtOH/THF (1:1), 503 nm; acetone, 482 nm; $H_2SO_4$, 498 nm (with strong hypochromicity that is indicative of a protonic substitution effect). Thus when the charges can be solvent stabilized, inter-unit stabilization/planarization is retarded and the absorption shifts hypsochromically. Likewise, stabilization of the polar ground state increases the energy gap of the $\pi-\pi^*$ transition which may exhibit charge transfer character.[3,14] Also notice that the visible

absorption drops sharply, with almost no tailing beyond 600 nm, a feature consistent with the near monodisperse polymeric nature.

When aqueous NaOH (0.05 M) was added dropwise to **7** in THF, the initial red-colored solution ($\lambda_{max}$ = 512 nm) became pale-orange and then finally brown ($\lambda_{max}$ = 881 nm) as more base was added (Figure 2). This pH-dependent shift in the absorption spectrum was reversible but
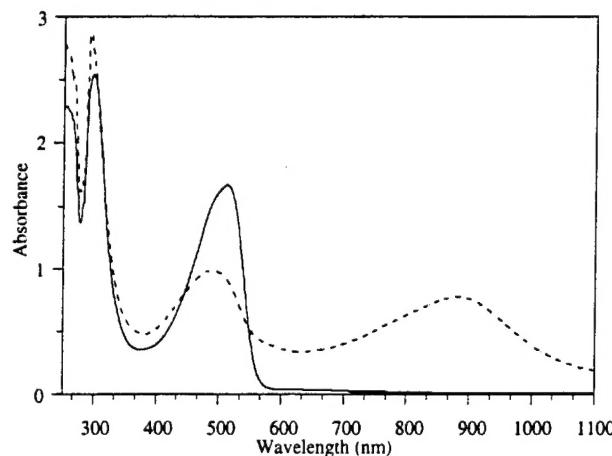


**Figure 2**. Spectrum of **7** (a) in THF (—) and (b) dissolution of **7** in THF/aqueous NaOH (- - -).

some polymer decomposition was detected after a few hours in the hydroxide-containing medium. When a milder base such as aqueous sodium bicarbonate (0.05 M) was added to **7** in THF, no polymer decomposition was observed after 50 h, and a reversible shift into the near-IR was still present. Equally impressive solution effects occurred upon the dissolution of **7** in strongly Lewis basic solvents[14] such as HMPA ($\lambda_{max}$ = 901 nm) or NMP ($\lambda_{max}$ = 746 nm) (**7** was insoluble in DMSO) (Figure 3).[15] No polymer decomposition was detected in these Lewis basic solvents.
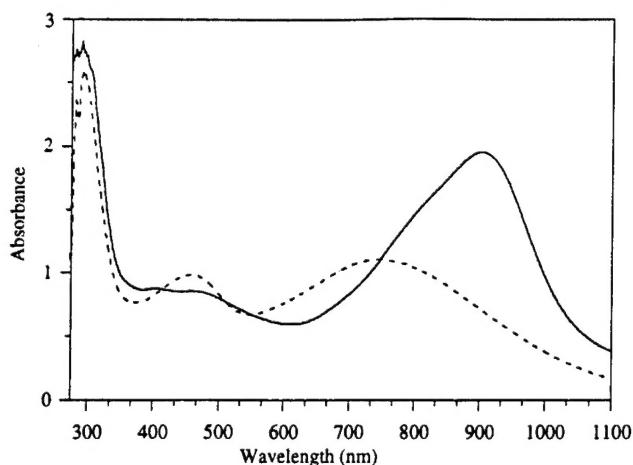
**Figure 3.** Spectrum of **7** in HMPA (—) and NMP (- - -) to form **9**.

There was no spectral difference with the strict exclusion of air, thus excluding an oxidative doping process. Upon the addition of aqueous HCl, the HMPA and NMP solutions once again became red with no absorption bands present above 600 nm. The $^{13}$C NMR spectrum of **7** in HMPA (with 10% CDCl$_3$ added for the lock) showed the butyl signals as well as a broad resonance from 176-163 ppm. In accord with the dramatic and reversible optical absorbance shifts, Brønsted or Lewis bases might be promoting a cascade of π-electron migrations in **7** to afford the planar conjugated polymer **9** (Scheme 1). **9** is similar to indigo (**10**) and indigo-like compounds (**11**)

**Scheme 1**
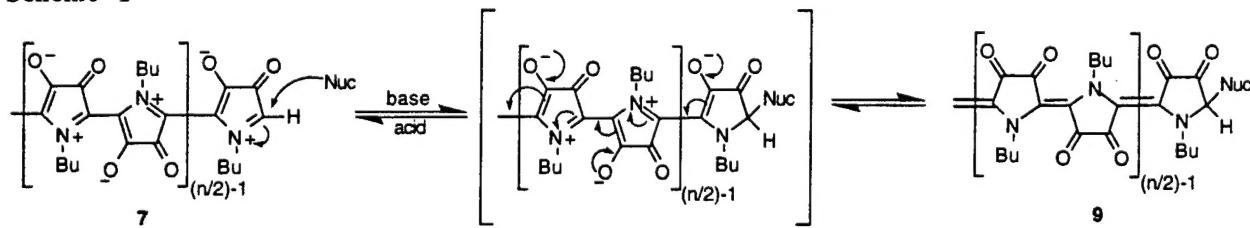


which possess extraordinarily large values of $\lambda_{max}$ for their small conjugation lengths; a feature which has been attributed to the cross-conjugated vinylogous amide moieties (Figure 4) .[3]

**10**
$\lambda_{max}$ = 602 nm

**11**
$\lambda_{max}$ = 528 nm
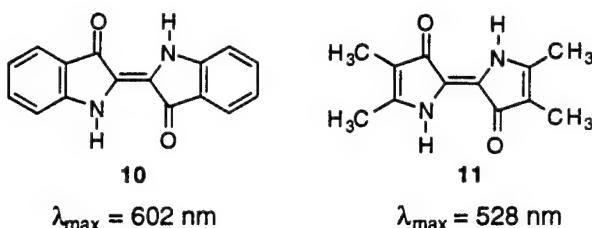
**Figure 4.** Indigo (**10**) and an indigo-like structure (**11**) that have a cross-conjugated vinylogous amide structure similar to that of **9**.

The solid diethylamine adduct ($\lambda_{max}$ in $Et_2NH$ solution = 783 nm) of **9** was obtained by removal of the excess amine under vacuum to afford a black powder. A pressed pellet of the powder had an intrinsic conductivity of $6.9 \times 10^{-5} \Omega^{-1} cm^{-1}$ and an iodine doped conductivity of $3.5 \times 10^{-3} \Omega^{-1} cm^{-1}$ (4-point probe). We were unable to form a free-standing film of the amine adduct.

Preliminary cyclic voltammetry (10 mV sec$^{-1}$, -1.0 to +1.0 V versus Ag/AgCl, 3 M Cl$^-$ at 20 °C) were consistent with a dramatic redox change under extremes of acidic and alkaline pH. When **7** was dissolved in $CH_3CN$, the dark brownish-black solution had an initial pH of 3.8 and the open circuit potential, $E_H$, was +0.12 V. Under these conditions, cyclic voltammetry revealed no noticeable redox features. When the pH was lowered to 1.1 by the addition of 2.0 M HCl, the solution immediately turned a clear mid-amber color and it established an open circuit potential of ca. +0.33 V. Under these conditions, cyclic voltammetry provided clear evidence of oxidation (-0.028 V, +0.681 µA) and reduction (-0.18 V, -2.15 µA) for a reaction that has an E$^{o'}$ of -0.10 V. There was also a second, non-reversible oxidation at ca. +0.9 V. When the pH of the solution was then raised to 11.4 with 1.0 M NaOH, the solution rapidly returned to a pH of 5.7. Further addition of base was necessary to maintain a pH at 12.7, indicating a considerable buffering capacity of the system. Under these conditions, cyclic voltammetry provided evidence for a new redox reaction. The redox transition at E$^{o'}$ = -0.10 V and the non-reversible oxidation at 0.9 V,

found under acidic conditions, were no longer evident. There was instead clear evidence for a non-reversible oxidation reaction at ca. 0.00 V. There was no evidence of film formation on the electrodes following the CV scans. These results are in agreement with a dramatic structural change in the polymer at varying pH levels.

Another interesting feature of **7** is that it could be partially reduced with $H_2$ (1 atm) over Pd/C (24 h, 23°C) to afford **12**, a polymer that was very similar to the starting polymer by FTIR and SEC analysis, while the $^1H$ NMR and $^{13}C$ NMR showed peak broadening; therefore, some of the units were hydrogenated. Although the reduced polymer cannot attain the degree of extended conjugation of **7** (as determined by the optical absorbances), its response range to different solvents can be from the UV region with weak tailing into visible, to the near-IR (DMSO, $\lambda = 886$ nm) (Figure 5).
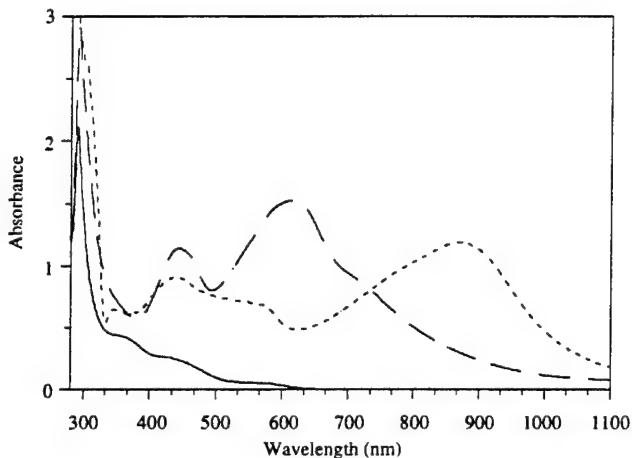


**Figure 5.** Spectrum of **12**, the reduction product of **7**, in (a) THF (—), (b) DMSO (- - -), and (c) THF/aqueous NaOH (— —).

It has been reported that polar aprotic solvents such as DMSO can tautomerize $N$-(methyl)pyrrol-3-one to $N$-(methyl)-3-hydroxypyrrole (eq 6).[16] Thus, there are two factors that may be

$$\text{(structure)} \xrightarrow[K_{enol} = 99.0]{\text{DMSO}} \text{(structure)} \quad (6)$$
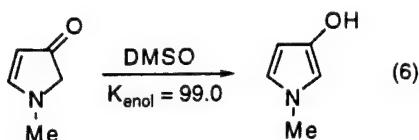
influencing the dramatic optical absorption range. First, as illustrated in Scheme 1, the nucleophilic additions on the zwitterionic units can afford indigo-like systems with extended conjugation. Second, in DMSO, extended conjugation may arise from the enol forms (eq 7).

$$\text{(structure 12)} \xrightleftharpoons[\text{THF}]{\text{DMSO}} \text{(structure)} \quad (7)$$

**12**
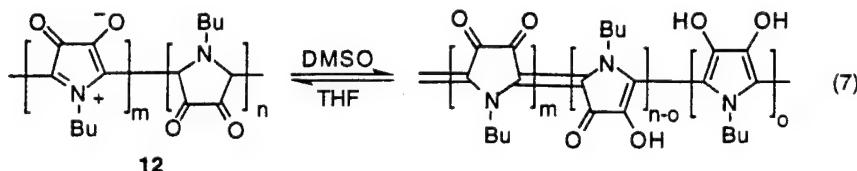
FTIR analysis substantiates this proposal in that **12** showed no -OH stretch in $CH_2Cl_2$; however, in DMSO, a strong -OH stretch was observed. It should be noted that the equilibrium between keto and enol forms in hydroxypyrroles are known to be highly solvent and substituent dependent.[7b] When aqueous NaOH (0.05 M) was added dropwise to **12** in THF, the initial yellow-colored THF solution became green, blue-green, and finally blue as more base was added and a new absorption band appeared at 618 nm (Figure 5). The absorption could be stabilized at any color along this transition depending on the amount of hydroxide added. Upon addition of aqueous HCl to the THF solution, the color moved back again over the same range before ceasing at the yellow-colored solution with a major absorption peak at < 290 nm. Unlike **7**, the reduced polymer **12** underwent no noticeable hydroxide-induced decomposition upon the reversible pH shifts.

We were able to dissolve **12** (0.05 wgt % relative to PVC plus plasticizer) in a solution of THF, poly(vinyl chloride) (PVC), and the plasticizer di(2-ethylhexyl)phthalate (DOP). Evaporation of the THF resulted in the formation of a dark green (possibly resulting from a mixture of yellow and blue)[3] transparent flexible film since DOP was acting as a Lewis base. Suspension of the film (250 μm thickness) in aqueous HCl (3 N) (no organic solvent was present)

caused the film to become bright yellow-orange while suspension in aqueous NaOH (0.5 M) caused the film to become dark blue-brown, and this process was reversible.

Since **7** was too brittle to form free-standing films, we were interested in the synthesis of an analogous system with a longer alkyl chain to decrease the crystallinity. Accordingly, dodecyl chains should promote little side chain crystallization and they may induce an internal plasticization.[1i,j] Our synthesis began with the preparation of *N*-dodecyl(pyrrole) **13** by treating pyrrole with 1-*n*-bromododecane in the presence of a phase transfer catalyst.[3] **13** was next brominated[4a] to afford **14** and oxidized using nitric acid to give the desired zwitterionic monomer **15**. Subsequent polymerization of **15** gave our desired polymer **16** ($M_n$ = 10,390; PD = 1.24) (eq 8).[13] The value of $\lambda_{max}$ for **16** was identical for that of **7** at 520 nm in $CCl_4$. When **16** was
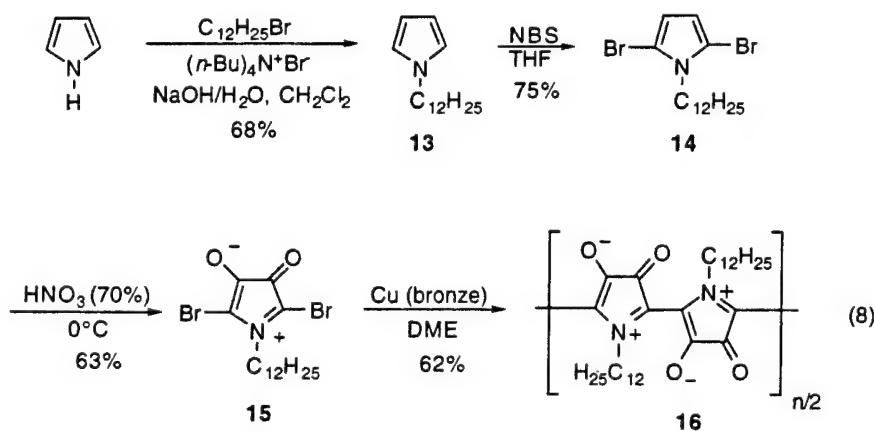


subjected to Lewis bases or Brønsted bases, the expected reversible shifts into the near-IR were observed (Figure 6). Moreover, from **16** we could obtain a flexible free-standing film cast from a
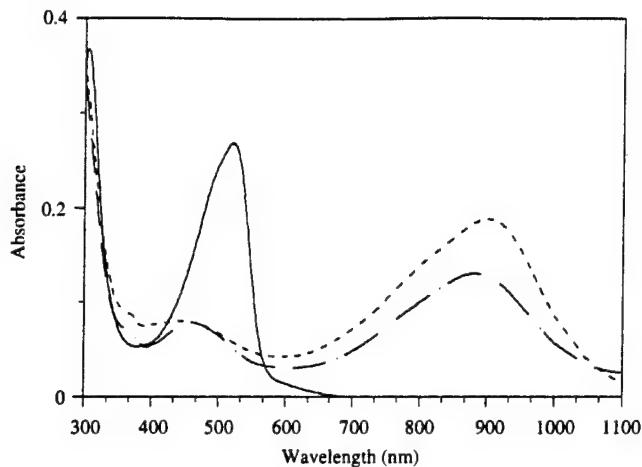
**Figure 6.** Spectrum of **16** in (a) CCl$_4$ (—), (b) THF/aqueous NaOH (— —) and (c) HMPA (- - -).

toluene solution. The maroon-colored film did not change its color when suspended in acid or base solutions. Apparently, the conformational change necessary was inaccessible in this solid form, or the dodecyl groups were providing a hydrophobic barrier to the aqueous solvent medium. Thus the aforementioned highly plasticized PVC-dissolved **12** was fluid enough to provide a unique composite structure for the needed structural changes. Our efforts to obtain conductivity measurements (4-point probe) on the film of **16** were hampered by repeated puncturing and subsequent cracking of the film.

Recently, Swager[2a] and McCullough[2b] reported the functionalization of polythiophenes with oligoethylene glycol (OEG) units to investigate the potential of tuning the electronic and/or photonic properties of polythiophenes via ion-dipole binding interactions. With a shift in the optical absorption, it was demonstrated that the geometry of the polymer's backbone was sensitive to the presence of salts. Likewise, we sought to investigate the ionochromic properties of our particularly dynamic zwitterionic polymer system by obtaining an *N*-OEG pyrrole monomer.

Triethylene glycol monomethyl ether was brominated to afford the OEG-Br.[17b] *N*-Alkylation of pyrrole with OEG-Br using standard phase transfer conditions[4a] gave us our alkylated pyrrole derivative (**17**) that was next brominated[5] and oxidized under our typical

conditions to afford the desired zwitterionic $N$-(OEG)pyrrolinium oxide derivative **19**. Polymerization of **19** using copper-bronze afforded the desired polymer **20** ($M_n = 8,650$, PD = 1.59)[13] in 59% after fractional precipitation (eq 9). We also attempted the polymerization of **19** in
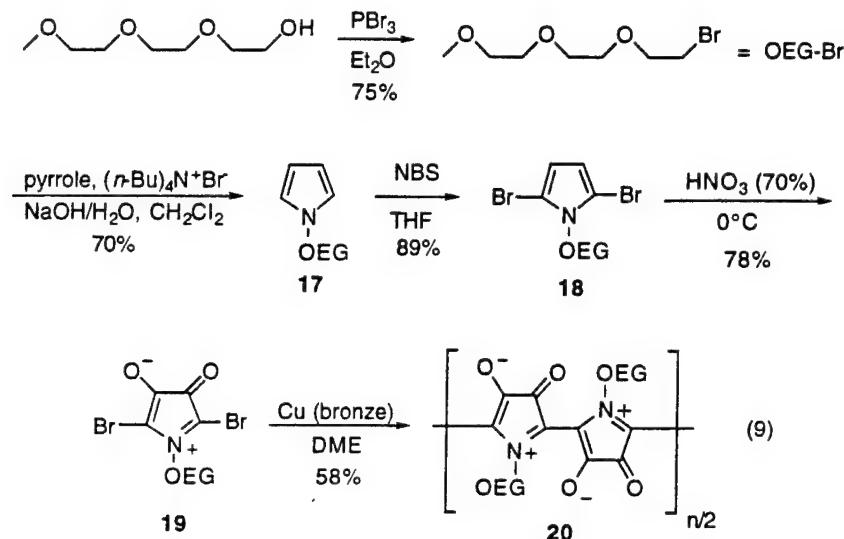


water, but the process yielded no polymeric material. As expected, **20** was water soluble and photonically responsive to Lewis and Brønsted bases (Figure 7). Distilled water induced a
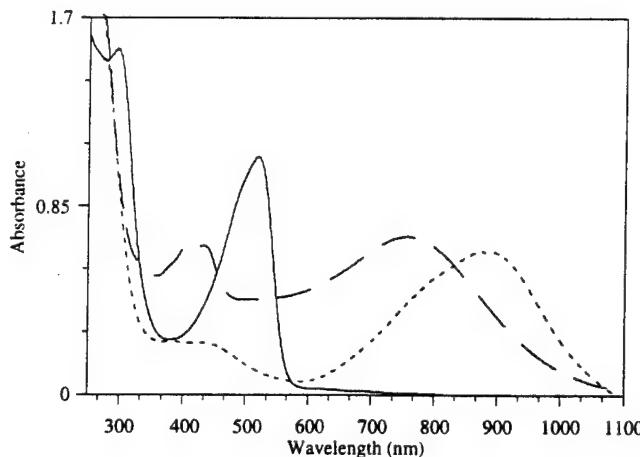


**Figure 7.** Spectrum of **20** in (a) CCl₄ (—), (b) THF/aqueous NaOH (— —), and (c) HMPA (- - -).

dramatic bathochromic shift of the optical absorption into the near-IR, however, in the presence of traces amount of HCl, no major absorption above 506 nm was observed (Figure 8).
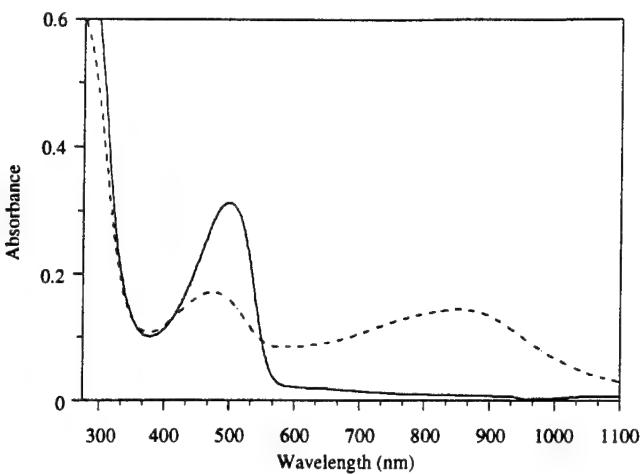
**Figure 8.** Spectrum of **20** in (a) distilled water (- - -), and (b) 0.1 N HCl (—).

To assess the ionochromism of **20**, all salt effect studies were conducted without water since, as shown in Figure 8, water can promote an absorption in the near-IR region. As listed in Table 1, we studied the affect of various-sized cations that had non-nucleophilic anions as well as

**Table 1**. Affect of Salts on the Optical Properties of **7** and **20**.

| Entry | Polymer | Solvent | Salt (0.2 M) | $\lambda$ (nm) |
|-------|---------|---------|--------------|----------------|
| 1 | **20** | MeOH | ——— | 484 |
| 2 | **20** | MeOH | $LiClO_4$ | 492 |
| 3 | **20** | MeOH | $NaClO_4$ | 488 |
| 4 | **20** | MeOH | $KClO_4$[a] | 488 |
| 8 | **20** | MeOH | $LiF$[a] | 487 |
| 9 | **20** | MeOH | $LiCl$ | 485 |
| 10 | **20** | MeOH | $LiBr$ | 484 |
| 11 | **20** | MeOH | $NaF$ | 486 |
| 12 | **20** | MeOH | $NaCl$[a] | 488 |
| 13 | **20** | MeOH | $NaBr$ | 489 |
| 14 | **20** | MeOH | $KF$ | 485 |
| 15 | **20** | MeOH | $KCl$[a] | 488 |

| 16 | 20 | MeOH | KBr[a] | 490 |
|----|----|------|--------|-----|
| 17 | 20 | MeOH | LiI | 480, 816 |
| 18 | 20 | MeOH | NaI | 459, 850 |
| 19 | 20 | MeOH | KI | 465, 876 |
| 20 | 20 | $CH_2Cl_2$ | ——— | 518 |
| 21 | 20 | $CH_2Cl_2$ | TBAI[b] | 518 |
| 22 | 20 | $CH_2Cl_2$ | $TMABF_4$[c] | 518 |
| 23 | 20 | $CH_2Cl_2$ | $TBAPF_6$ | 517 |
| 24 | 20 | MeOH/THF (9:1) | ——— | 493 |
| 25 | 20 | MeOH/THF (9:1) | LiI | 476, 818 |
| 26 | 20 | MeOH/THF (9:1) | NaI | 474, 850 |
| 27 | 20 | MeOH/THF (9:1) | KI | 458, 863 |
| 28 | 7 | MeOH/THF (9:1) | ——— | 480 |
| 29 | 7 | MeOH/THF (9:1) | LiI | 477 |
| 30 | 7 | MeOH/THF (9:1) | NaI | 479 |
| 31 | 7 | MeOH/THF (9:1) | KI | 478 |
| 32 | 7 | $CH_2Cl_2$ | ——— | 518 |
| 33 | 7 | $CH_2Cl_2$ | TBAI | 516 |
| 34 | 7 | MeOH/THF (9:1) | NaI + 18-C-6 | 487 |
| 35 | 7 | MeOH/THF (9:1) | KI + 18-C-6 | 486 |

[a]This salt was only partially dissolved in MeOH. [b]TBA= tetrabutylammonium. [c]TMA = tetramethylammonium.

cations that had nucleophilic counter ions, in an attempt to differentiate between a cationic or anionic (nucleophilic) effect. **20** might dramatically change its conformation through a nucleophilic attack as shown for **7** (Scheme 1), and/or further by a cation chelation as shown in Scheme 2. Note that such a chelation, depending on the conformation, could vary the equilibrium

**Scheme 2**
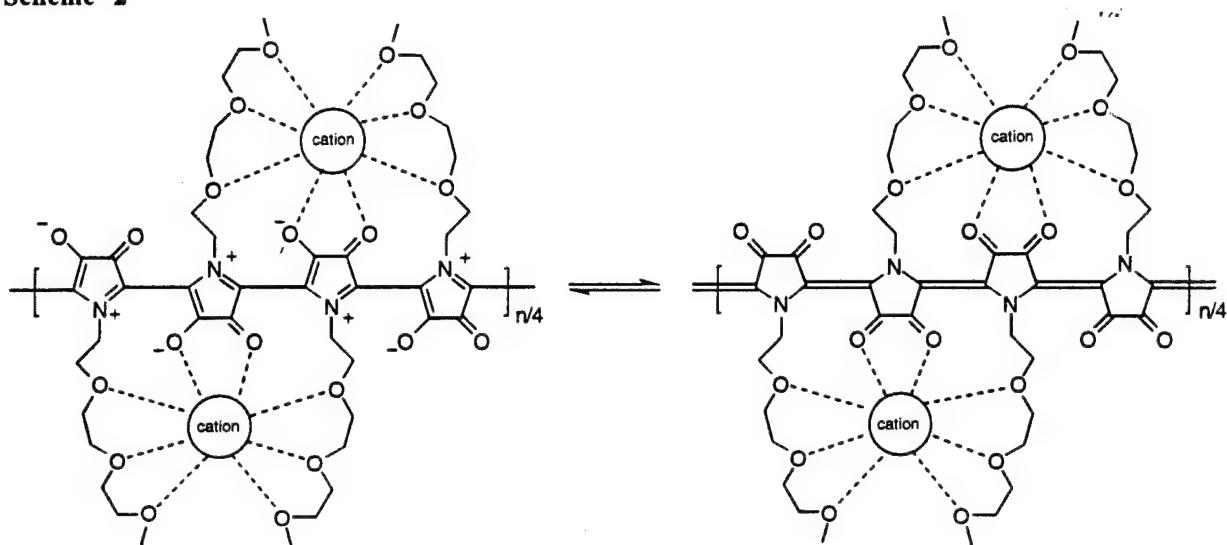


to enhance or retard the planarization process. The diameter of the cavity between alternating OEG units in the planarized system, as depicted in Scheme 2, was calculated to be 3-5 Å using a modified MM2 force-field on a tetramer. This cavity size is easily adjustable due to the flexibility of the OEG units, thus this computation merely suggested that the proper cavity sizes for such ion captures were attainable. The studies in MeOH indicate that only iodide-containing salts could induce an absorption in the near-IR (Table 1, entries 17-19, and 25-27) (Figure 9).
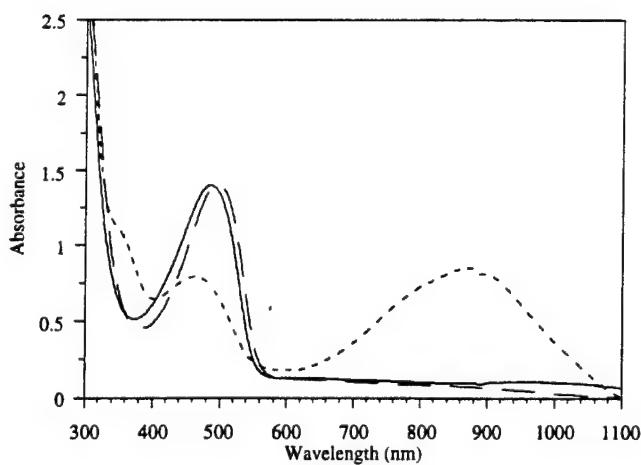


**Figure 9.** Spectrum of **20** in (a) MeOH (——), (b) 0.2 M KBr/MeOH (— —), and (c) 0.2 M KI/MeOH (- - -).

*Remarkably, this polymeric system was completely iodide-specific (iodochromic); there was no absorption in the near-IR with the corresponding chloride or bromide salts.* This is likely a testimony of the enhanced nucleophilicity of iodides over that of the other halogens in polar protic solvents. The small halogens are more nucleophilic than the larger halogens when dissolved in polar aprotic solvents such as DMSO, however, since the polar aprotic solvents themselves induce the near-IR shifts, studies in these solvents were not conducted. The more ionic the iodide salt, $Li^+ < Na^+ < K^+$ (Table 1, entries 17-19 and 25-27), the greater the iodide nucleophilicity and the greater the bathochromic shift of the near-IR bands, thus signifying greater formation of the planar form (moving the equilibrium to the right in Scheme 2). Likewise, there was a corresponding greater hypsochromic shift in the visible absorption band for NaI and KI over that of the LiI, signifying a smaller amount of the non-planar form being present for NaI and KI. The anion alone is not the only component that is necessary for the ion-induced conformational planarization and formation of the near-IR absorption band. This is clearly seen by studying the affect of LiI, NaI, and KI on the butyl polymer **7**, which, though not very soluble in MeOH, is soluble in a 9/1 mixture of MeOH/THF (Table 1, entries 29-31). (Note that TMAI and TBAI are insoluble in MeOH.) There was no affect of LiI, NaI, and KI on the optical absorption of **7**. Therefore, for these zwitterionic polymers to be dramatically ionochromic, affording a new absorption in the near-IR spectral region, the anion must be a good nucleophile and there must be a location for cation capture. We further substantiated this mechanistic interpretation by adding KI and NaI to **7** in MeOH/THF in the presence of 18-crown-6 (Table 1, entries 34 and 35). The iodide is far more nucleophilic under these conditions since cation capture by the crown ether can occur. However, there was little change in the spectral properties of **7** under these conditions. Thus the OEG units provide unique cation capture sites on **20** to maintain a significant portion of the planarized form after iodide attack. Exogenous crown ethers do not have the same effect on the planarization process.

We were interested in the preparation of AB-type polymers using monomer **8** in order to evaluate their corresponding optical-based sensory affects. We first investigated a Pd(0)-catalyzed cross coupling of **8** with an arylboronic ester;[18] however, only monomer decomposition was observed, even in the absence of base or catalyst. In light of these initial results, we switched to the Pd(0)-catalyzed cross coupling of our monomer with arylstannanes.[19] We explored the efficacy of this coupling procedure by first using a model system. When using triphenylphosphine as the supporting ligand for the Pd(0), coupling of **8** with phenyltributylstannane,[20] we again observed monomer decomposition. Conversely, by using modified-Stille coupling conditions[21] where the less nucleophilic triphenylarsine was used as a supporting ligand, we were able to generate our desired product (**21**) in 90% yield (eq 10). Though this yield is still too low to expect
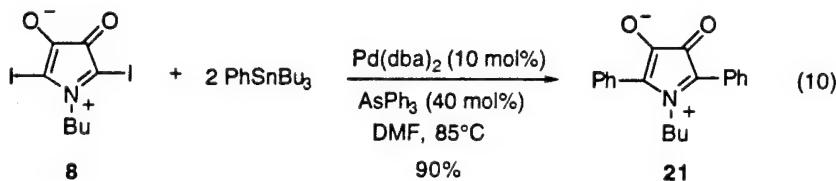
any significant degree of polymerization by a step-growth process, we proceeded to prepare the oligomeric system to study the optical properties. 1,4-Bis(tri-$n$-butylstannyl)benzene[22] was coupled with **8** using analogous coupling conditions, and we obtained oligomer **22** with $M_n <$ 1,800 and yields between 17-54%; however, by changing the solvent to toluene and increasing the reaction temperature from 65° to 120°, our yield increased to 89% with $M_n = 2,010$ (eq 11).[13]
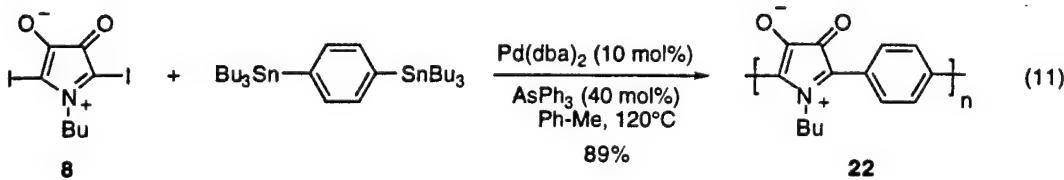
Although aryl(trimethyl)stannanes might transmetalate more efficiently than the tributyl derivatives, no increase in the yield or degree of polymerization was attained when we used 1,4-

bis(trimethylstannyl)benzene.[23] **22** was soluble in common organic solvents and exhibited a $\lambda_{max}$ at 410 nm in THF (Figure 10). **22** did not exhibit a reversible bathochromic shift when
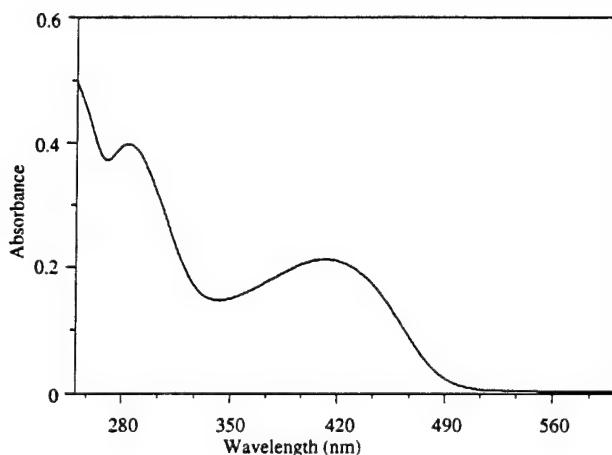


**Figure 10.** Spectrum of **22** in THF.

dissolved in Lewis bases or when subjected to a Brønsted base in THF; thus, the energy difference for the 1,4-phenylene moiety to isomerize to the quinoidal form is apparently too great for long-range backbone planarization to occur.

In summary, we have described the synthesis of novel zwitterionic pyrrole-derived monomers which, upon polymerization, afforded unique polymers that can undergo reversible optical shifts from the visible to the near-IR with a solution band gap of approximately 1.1 eV. This low band-gap is the result of a structural change from the zwitterionic form to an indigo-like form which can be induced by Lewis or Brønsted bases, and the planarization is reversible upon the addition of acid. Furthermore, the polymer can be modified through a Pd/$H_2$ reduction to give a polymer with a greater spectral absorbance range, from the near-UV to the near-IR, when dissolved in Lewis or Brønsted bases. Free-standing films of the polymer can be generated by functionalizing the monomer with a dodecyl chain. When functionalized with oligoethylene glycol units, the polymer was water soluble, and it exhibited a reversible ionochromic response, specifically, only an iodochromic response, from the visible to the near-IR. Finally, using

modified Stille coupling conditions, we showed that low molecular weight AB-type polymers can be synthesized from this zwitterionic monomer. However, the energy needed to convert the phenylene units into their quinoidal forms was sufficient to retard the extended planarization process.

## Experimental

**General Procedures.** All non-aqueous operations were carried under a dry, oxygen free, nitrogen atmosphere. Proton NMR spectra were recorded at 300, 400 or 500 MHz on Brüker AM-300, Varian 400, or Brüker AM-500 spectrometers, respectively. The $^{13}$C NMR spectra 75, 100 or 125 MHz were recorded on Brüker AM-300, Varian 400, or Brüker AM-500 spectrometers, respectively. Proton chemical shifts ($\delta$) are reported in ppm down field from tetramethylsilane (TMS) and $^{13}$C resonances were recorded using the 77.0-ppm CDCl3 resonance of the solvent as an internal reference and are reported in ppm down field from TMS. Infrared (FTIR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. The accurate-mass spectra were determined on a VG Analytical, Ltd., 70SQ high resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091, or Galbraith Laboratories, Inc., P.O. Box 51610, Knoxville, TN 37950-1610. Capillary GC analyses were obtained using a Hewlett Packard Model 5890 Series II gas chromatograph equipped with and Alltech model 932525 (25 m x 0.25 mm, 0.2 μm film of AT-1 stationary phase) capillary GC column and a Hewlett Packard 3396 Series II integrator. Ultraviolet and visible (UV-Vis) spectra were recorded using a Perkin Elmer UV/Vis Lambda 2S Spectrometer. Luminescence spectra were recorded using a Perkin Elmer Luminescence LS 50B Spectrometer. Size exclusion chromatography was recorded using a Waters 150-C Gel Permeation Chromatograph equipped with two, in series, 30 x 75 cm Burdick and Jackson GPC columns ($10^5$ Å, 10 μm and 500 Å, 5 μm) maintained at 60°C with THF as the eluant and a Waters 486 Tunable Absorbance Detector. Copper bronze was purchased from Aldrich Chemical Company. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade 1,2-dimethoxyethane (DME) and benzene were distilled under nitrogen from sodium. Reagent grade dichloromethane, toluene, hexamethylphosphoramide (HMPA), dimethylsulfoxide (DMSO) and 1-methyl-2-pyrrolidinone (NMP) were distilled under nitrogen from CaH$_2$. Bulk grade hexane was distilled prior to use. Gravity column chromatography and flash chromatography were carried out

on silica gel (230-400 mesh from EM Science). Conductivity measurements were obtained using an Alessi CPS-05 Contact Probe Station, a Keithley Model 224 Programmable Current Source and a Keithley 169 Digital Multimeter. Cyclic voltammograms were obtained using an EG&G Model 273 Potentiostat/Galvanostat. If a compound has previously been reported, a reference to that compound is shown directly after the compound number in the title of the synthetic procedure. The pyrrole systems, prior to $HNO_3$ oxidation, were oxidatively unstable and they were used immediately after preparation. ^{1}H NMR integrals in the alkyl region were rounded to the nearest integer unit. Integrals of ^{1}H NMR resonances that merged with the water resonance in the $CDCl_3$, were reported as the number of protons consistent with the alkyl moiety present in that region of the spectrum.

*N*-(*n*-**Butyl**)**pyrrole** (**1**).[4b] The procedure by Wang[4a] was modified as follows. A nitrogen purged flask equipped with a reflux condenser was charged with methylene chloride (100 mL), tetrabutylammonium bromide (32.24 g, 100.0 mmol), pyrrole (7.63 mL, 100 mmol) and 1-bromo-*n*-butane (11.81 mL, 110.0 mmol) and the mixture was cooled to 0°C using an ice bath. To this solution was added dropwise 50% aqueous sodium hydroxide (100 mL). After addition, the reaction mixture was heated to reflux and allowed to stir for 24 h. The mixture was cooled and diluted with water (50 mL) and the aqueous phase was extracted with methylene chloride (3x). The combined organic extracts were washed with 3 N hydrochloric acid, water, brine, and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography [silica gel, hexanes/ether (9:1)] to afford 11.0 g (90%) of the title compound as a yellow liquid. FTIR (film) 3097, 2959, 1538, 1500, 1462, 1374, 1282, 1088, 1061, 959, 719 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (t, J = 2.0 Hz, 2 H), 6.12 (t, J = 2.0 Hz, 2 H), 3.85 (t, J = 7.2 Hz, 2 H), 1.73 (p, J = 7.3 Hz, 2 H), 1.30 (sext, J = 7.7 Hz, 2 H), 0.92 (t, J = 7.3 Hz, 3 H).

*N*-(*n*-**Butyl**)-**2,5-dibromopyrrole** (**2**). The procedure used was analogous to Khoury's[5] method and was modified as follows. To a nitrogen purged flask charged with THF (100 mL) was added **1** (0.90 g, 7.31 mmol) and the mixture was then cooled to -78°C. To this

solution was added *N*-bromosuccinimide (2.60 g, 14.6 mmol) and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 16 h, the solvent was removed *in vacuo* from the mixture, and the crude product was dissolved in ether and filtered. The solvent was removed from the filtrate to give a residue that was purified by flash chromatography (silica gel, hexanes) to afford 1.64 g (80%) of the title compound as a clear white liquid. FTIR (film) 3133, 2959, 2867, 1638, 1501, 1454, 1418, 1372, 1279, 1213, 1105, 997, 941, 895, 741 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 6.14 (s, 2 H), 3.94 (t, J = 7.6 Hz, 2 H), 1.64 (p, J = 7.4 Hz, 2 H), 1.34 (sext, J = 7.6 Hz, 2 H), 0.94 (t, J = 7.4 Hz, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 103.70, 102.09, 50.86, 33.02, 20.53, 14.60.

**$N$-($n$-Butyl)-2,5-dibromo-3-oxopyrrolinium-4-oxide (3).** A flask equipped with an internal thermometer was charged with nitric acid (20 mL, 70 %) and the solution was cooled to 0°C. To this solution was added dropwise **2** (15.58 g, 55.34 mmol) over a period of 20 min without allowing the temperature to rise above 35°C. After addition, the mixture was allowed to stir an additional 15 min at 0°C and then poured onto ice. The aqueous phase was extracted with ethyl acetate (3x) and the combined organic extracts were washed with brine. The organic phase was dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chromatography [silica gel, hexanes/ether (8:2)] to give a yellow solid which was recrystallized from ethanol to afford 11.53 g (67%) of the title compound as yellow crystals. FTIR (KBr) 2923, 2851, 1718, 1589, 1461, 1441, 1389, 1348, 1323, 1153, 1046, 933, 830 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 3.59 (t, J = 7.3 Hz, 2 H), 1.57 (p, J = 7.1 Hz, 2 H) 1.30 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 164.02, 129.41, 39.65, 30.56, 19.99, 13.69. LRMS calc'd for C$_8$H$_9$Br$_2$NO$_2$: 311. Found: 311. Anal. calc'd for C$_8$H$_9$Br$_2$NO$_2$: C, 30.89; H, 2.92; Br, 51.39; N, 4.50. Found: C 30.90; H, 2.92; Br, 51.25; N, 4.48. Mp. 74 - 76°C. λ (CH$_2$Cl$_2$) = 248, 322 nm. λ (NMP) = 281 nm. λ (THF/aqueous NaOH) = 241, 314 nm. λ (THF/3 N HCl) = 240, 315 nm.

**$N$-($n$-Butyl)-2,5-dibromo-4-hydroxypyrrol-3-($2H$)-one (4).** To a nitrogen purged flask charged with methanol (15.0 mL) was added at 0°C sodium borohydride (0.15 g, 8.0

mmol). The mixture was allowed to stir until all the sodium borohydride was dissolved. To this solution was added at 0°C **3** (1.24 g, 4.00 mmol) and the reaction was allowed to warm to room temperature. After stirring at room temperature for 15 min, the reaction mixture was acidified with 3 N hydrochloric acid (10 mL) and the aqueous phase was extracted with ether (3x). To the combined organic extracts was added NaOH (10 mL, 2 M) and the aqueous phase was washed with ether. The alkaline phase was then acidified with hydrochloric acid (3 N) and the aqueous phase was extracted with ether (3x). The combined organic extracts were dried over sodium sulfate and the solvent was removed *in vacuo* to afford 0.68 g (55%) of the title compound as a white solid that was not purified. FTIR (KBr) 3324, 2961, 2932, 2873, 1697, 1617, 1428, 1312, 1246, 1152, 1108, 1057 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.26 (br s, 2 H), 3.52 (m, 1 H), 3.27 (m, 1 H), 1.54-1.46 (m, 2 H), 1.26 (sext, J = 7.5 Hz, 2 H), 0.87 (t, J = 7.3 Hz, 3 H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 163.82, 139.43, 121.80, 84.59, 40.61, 30.42, 20.18, 13.83. LRMS calc'd for C$_8$H$_{11}$Br$_2$NO$_2$: 313. Found: 313.

**Compound 5 or 6.** A nitrogen purged flask equipped with a reflux condenser was charged with benzene (1.0 mL), cyclopentadiene (0.091 mL, 1.00 mmol) and **3** (0.311g, 1.00 mmol). The reaction mixture was heated to reflux and allowed to stir for 24 h. The mixture was cooled, and after removal of solvent *in vacuo*, the crude product was purified by flash chromatography [silica gel, hexanes/ether (7:3)] to afford 0.383 g (100%) of the title compound as a white solid. FTIR (KBr) 2967, 2944, 2876, 1781, 1713, 1441, 1911, 1362, 1210, 1065, 912, 730, 694 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 6.17 (t, J = 1.9 Hz, 2 H), 3.51 (p, J = 1.9 Hz, 2 H), 3.41 (t, J = 7.3 Hz, 2 H), 2.56 (dt, J = 9.7, 1.4 Hz, 1 H), 2.18 (dt, J = 9.7, 1.6 Hz, 1 H), 1.45 (p, J = 7.5 Hz, 2 H), 1.26 (sext, J = 8.3 Hz, 2 H), 0.89 (t, J = 7.2 Hz, 3 H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 171.59, 136.39, 66.77, 56.27, 50.96, 39.72, 29.33, 19.98, 13.61. LRMS calc'd for C$_{13}$H$_{15}$Br$_2$NO$_2$: 377. Found (CI, NH$_3$): 378 (M+H), 395 (M+NH$_4$). Mp. 112 - 115°C.

**Poly-*N*-(*n*-butyl)-3-oxopyrrolinium-4-oxide (7).** To a dry nitrogen purged screw-cap reaction tube charged with DME (1.5 mL) was added **3** (0.155 g, 0.500 mmol) and copper bronze (0.254 g, 4.00 mmol). The reaction tube was sealed and heated to 200°C for 24 h

and then allowed to cool to 23°C. The crude reaction product was taken up in methylene chloride and filtered. Solvent was removed from the filtrate *in vacuo* to give a residue which was dissolved in methylene chloride and fractionally precipitated by the addition of methanol to afford 42.0 mg (56%) of the title compound as a maroon solid. FTIR (film) 2943, 2861, 1769, 1697, 1435, 1400, 1359, 1333, 1184, 1102, 1030, 928, 702 cm$^{-1}$. FTIR (Et$_2$NH adduct, KBr) 2964, 2872, 2933, 1707, 1507, 1435, 1400, 1364, 1179, 1107, 1046, 933, 748 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 3.48 (br s, 2 H), 1.55 (br s, 2 H), 1.27 (br s, 2 H), 0.89 (br t, J = 7.5 Hz, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 169.61, 131.52, 39.71, 31.03, 20.53, 14.37. $^{13}$C NMR (125 MHz, HMPA/ 10% CDCl$_3$) δ 177-164, 21.21, 14.70, other two *n*-butyl resonances under HMPA resonance. $M_n$ = 3,910. $M_w/M_n$ = 1.25. Anal. calc'd for (C$_8$H$_9$NO$_2$)$_n$: C, 63.56; H, 6.00; N, 9.26. Found: C, 63.40; H, 6.71; Br, <0.5; Cu, <0.02; N, 8.06. Intrinsic Conductivity (4-point probe, pellet) 1.44 x 10$^{-5}$ Ω$^{-1}$cm$^{-1}$. Iodine doped (4-point probe, pellet) 4.2 x 10$^{-4}$ Ω$^{-1}$cm$^{-1}$. Intrinsic Conductivity (Et$_2$NH adduct, 4-point probe, pellet) 6.9 x 10$^{-5}$ Ω$^{-1}$cm$^{-1}$. Iodine doped (Et$_2$NH adduct, 4-point probe, pellet) 3.46 x 10$^{-3}$ Ω$^{-1}$cm$^{-1}$. λ$_{max}$ (CCl$_4$) = 520 nm. λ$_{max}$ (CH$_2$Cl$_2$) = 518 nm. λ$_{max}$ (THF) = 512 nm. λ$_{max}$ [EtOH/THF (1:1)] = 503 nm. λ$_{max}$ (acetone) = 482 nm. λ$_{max}$ (NMP) = 459, 746 nm. λ$_{max}$ (HMPA) = 901 nm. λ$_{max}$ (Et$_2$NH) = 392, 783 nm. λ$_{max}$ (THF/aqueous NaOH) = 489, 881 nm. ε$_{max}$(CH$_2$Cl$_2$) based on monomer unit = 4,300 M$^{-1}$cm$^{-1}$. λ$_{max}$ (H$_2$SO$_4$) = 498 nm; ε$_{max}$ (H$_2$SO$_4$) based on monomer unit = 2,400 M$^{-1}$cm$^{-1}$. Florescence (CH$_2$Cl$_2$): emission at 569.5 nm.

**$N$-($n$-Butyl)-2,5-diiodo-3-oxopyrrolinium-4-oxide  (8).**  The procedure by Abraham[14] was modified as follows. To a dry nitrogen purged screw-cap reaction tube charged with acetone (50 mL) was added sodium iodide (5.98 g, 39.9 mmol) and **3** (1.24 g, 3.99 mmol). The reaction tube was sealed and heated to 80°C for 18 h and then allowed to cool to 23°C. The crude product was filtered through a plug of silica gel (ether) and the solvent was removed from the filtrate, *in vacuo*, to give a solid that was recrystalized from ethanol to afford 1.59 g (99%) of the title compound as orange crystals. FTIR (KBr) 2963, 2934, 1764, 1706, 1546, 1452, 1393, 1364, 1335, 1314, 1132, 1037, 928, 798, 725 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 3.59 (t, J =

7.2 Hz, 2 H), 1.54 (p, J = 7.1 Hz, 2 H), 1.27 (sext, J = 8.0 Hz, 2 H), 0.89 (t, J = 7.3 Hz, 3 H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 166.47, 117.33, 40.09, 30.59, 19.92, 13.62. HRMS calc'd for C$_8$H$_9$NI$_2$O$_2$: 404.8723. Found: 404.8713. Anal. calc'd for C$_8$H$_9$NI$_2$O$_2$: C, 23.72; H, 2.23; N, 3.34; I, 62.67. Found: C 23.92; H, 2.25; N, 3.45; I, 62.58. Mp. 104 -107°C.

**Polymer 12**. To a flask charged with methylene chloride (100 mL) was added **7** (0.10 g, 0.66 mmol) and 10% Pd/C (0.070 g). The flask was fitted with a hydrogen balloon and the reaction mixture was allowed to stir for 24 h at 23°C. The reaction mixture was taken up with methylene chloride and filtered. Solvent was removed from the filtrate *in vacuo* to give a residue that was dissolved in minimal amount of methylene chloride and fractionally precipitated by the addition of methanol to afford 0.089 g (89%) of the title compound as a viscous yellow liquid. FTIR (film) 3466, 2964, 2871, 1774, 1697, 1441, 1405, 1359, 1359, 1287, 1266, 1189, 1066, 1082, 928, 738, 687 cm$^{-1}$. FTIR (DMSO) 3435, 2882, 1646, 1461, 1261, 1292, 1200, 1061, 984, 743 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 3.44 (br s, 2 H), 1.52 (br s, 2 H), 1.23 (br s, 2 H), 0.87 (br s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 173-169, 140-131, 45-38, 31.03, 30.14, 20.78, 14.36. $M_n$ = 3190. $M_w/M_n$ = 1.6. Anal. calc'd for **7** (C$_8$H$_9$NO$_2$)$_n$: C, 63.56; H, 6.00; N, 9.26. Found for the reduction product of **7**: C, 58.95; H, 6.26; N, 8.06. $\lambda_{max}$ (THF) = 290 nm. $\lambda_{max}$ (THF/aqueous NaOH) = 444, 618 nm. $\lambda_{max}$ (DMSO) = 440, 886 nm.

**Polymer 12-PVC-DOP film.** To a dry, nitrogen purged beaker was added polymer **12** (9.7 mg) and THF (20 mL). The solution was allowed to stir until all the polymer was dissolved. To this solution was added medium molecular weight polyvinylchloride (0.9 g, Aldrich) and di(2-ethylhexyl)phthalate (2.1 g, 5.37 mmol). The combined substrates were heated gently to afford a homogeneous clear solution. The hot solution was then poured into a dry nitrogen purged glass recrystalization dish which was subsequently covered with paper towels and two heavy books to allow slow evaporation of the THF. After 24 h, the composite was peeled from the dish as a green transparent elastic film. The film was suspended in 3 N hydrochloric acid, and after a period of 5 h the color had changed to yellow. Suspension of the yellow film in 1 M NaOH changed the color to blue/brown, and this process was reversible.

*N*-**Dodecylpyrrole (13).**[4c] The procedure by Wang[4a] was modified as follows. A nitrogen purged flask equipped with a reflux condenser was charged with methylene chloride (100 mL), tetrabutylammonium bromide (48.36 g, 150.0 mmol), pyrrole (10.40 mL, 150.0 mmol) and 1-bromododecane (24.0 mL, 100 mmol), and the mixture was cooled to 0°C using an ice bath. To this solution was added dropwise 50% sodium hydroxide (100 mL). After addition, the reaction mixture was heated to reflux and allowed to stir for 24 h. The mixture was cooled and diluted with water (50 mL) and the aqueous phase was extracted with methylene chloride (3x). The combined organic extracts were washed with 3 N hydrochloric acid, water, brine, and dried over sodium sulfate. The solvent was removed *in vacuo*, and the crude product was purified by flash chromatography [silica gel, hexanes/ether (9:1)] to afford 16.04 g (68%) of the title compound as a yellow liquid. FTIR (film) 3107, 2912, 2851, 1533, 1497, 1461, 1369, 1276, 1087, 1061, 964, 717 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 6.63 (t, J = 2.1 Hz, 2 H), 6.11 (t, J = 2.1 Hz, 2 H), 3.84 (t, J = 7.2 Hz, 2 H), 1.73 (m, 2 H), 1.23 (br s, 18 H), 0.86 (t, J = 6.9 Hz, 3 H).

*N*-**Dodecyl-2,5-dibromopyrrole (14)**. The procedure used was analogous to Khoury's[5] method which was modified as follows. A nitrogen purged flask was charged with **13** (16.04 g, 68.30 mmol) and THF (250 mL) and the mixture was cooled to -78°C. To this solution was added *N*-bromosuccinimide (24.30 g, 136.6 mmol) and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 16 h, the solvent was removed *in vacuo*, and the crude product was taken up in ether and filtered. The solvent was removed from the filtrate to give a residue that was purified by flash chromatography (silica gel, hexanes) to afford 20.13 (75%) of the title compound as a clear liquid. FTIR (film) 3134, 2920, 2856, 1498, 1456, 1424, 1376, 1295, 1109, 1066, 996, 948, 900, 740 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 6.13 (s, 2 H), 3.92 (t, J = 7.7 Hz, 2 H), 1.65 (m, 2 H), 1.24 (m, 18 H), 0.86 (t, J = 6.9 Hz, 3 H).

*N*-**Dodecyl-2,5-dibromo-3-oxopyrrolinium-4-oxide (15).** A flask equipped with an internal thermometer was charged with nitric acid (50 mL, 70%) and cooled to 0°C by means of an ice bath. To this solution was then added dropwise **14** (12.59 g, 32.00 mmol) over a

period of 20 min without allowing the temperature to rise above 35°C. After the addition was complete, the mixture was poured onto ice. The aqueous phase was extracted with ethyl acetate (3x) and washed with brine. The combined organic extracts were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chromatography [silica gel, hexanes/ether (94:6)] to give a yellow solid which was recrystallized from ethanol to afford 8.52 g (63%) of the title compound as yellow crystals. FTIR (KBr) 2911, 2844, 1777, 1716, 1594, 1466, 1438, 1394, 1355, 1150, 1061, 1016, 866, 811 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.57 (t, J = 6.8 Hz, 2 H), 1.57 (p, J = 6.8 Hz, 2 H), 1.22 (m, 18 H), 0.85 (t, J = 6.7 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.887, 129.31, 39.83, 31.96, 29.66 (2C), 29.59, 29.47, 29.38, 29.11, 28.47, 26.67, 22.73, 14.17. HRMS calc'd for C$_{16}$H$_{25}$Br$_2$NO$_2$: 421.0252. Found: 421.0244. Anal. calc'd for C$_{16}$H$_{25}$Br$_2$NO$_2$: C, 45.41; H, 5.95; N, 3.31. Found: C 45.49; H, 5.95; N, 3.33. Mp = 50°-53°C.

**Poly-*N*-dodecyl-3-oxopyrrolinium-4-oxide (16).** To a dry nitrogen purged screw-cap reaction tube charged with DME (1.5 mL) was added **15** (0.115 g, 0.270 mmol) and copper bronze (0.26 g, 4.0 mmol). The reaction tube was sealed and heated to 200°C for 48 h and then allowed to cool to 23°C. The crude reaction product was taken up in methylene chloride and filtered. Solvent was removed from the filtrate *in vacuo* to give a residue which was dissolved in methylene chloride and fractionally precipitated by the addition of methanol to afford 0.044 g (62%) of the title compound as a maroon solid. FTIR (film) 2923, 2851, 1728, 1697, 1441, 1405, 1369, 1159, 1107, 1041 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 3.46 (br s, 2 H), 1.53 (br s, 2 H), 1.23 (br s, 18 H), 0.84 (br s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 169.47, 131.46, 40.06, 32.68, 31.66, 30.46, 30.43, 30.31, 30.25, 30.12, 29.02, 27.43, 23.44, 14.84. $M_n$ = 10,390. $M_w/M_n$ = 1.24. Anal. calc'd for (C$_{16}$H$_{25}$NO$_2$)$_n$ : C, 72.96; H, 9.56; N, 5.31. Found : C, 71.47; H, 9.58; Br, <0.5; N, 4.94. $\lambda_{max}$ (CCl$_4$) = 520 nm. $\lambda_{max}$ (CH$_2$Cl$_2$) = 503 nm. $\lambda_{max}$ (NMP) = 448, 790 nm. $\lambda_{max}$ (HMPA) = 447, 900 nm. $\lambda_{max}$ (THF/aqueous NaOH) = 488, 790 nm.

**Polymer 16 Film.** To a 2.5 mL vial was added **16** (0.08 g) and toluene (0.1 mL). The polymer solution was added onto a glass plate and slow evaporation (3 days) of toluene in a

desiccator gave a film on glass which was first carefully dried with a hairdryer and then residual solvent was removed *in vacuo*. The glass-support film was suspended in MeOH (100 mL) for 1 day. Evaporation of MeOH at room temperature and careful removal of the film from the glass plate with a razor blade afforded a flexible free standing film of the title compound.

**2-(Ethoxy ethoxy methoxy)ethyl bromide.**[17a] The procedure by McMurry[17b] was modified as follows. A dry, nitrogen purged flask was charged with ether (10 mL) and triethylene glycol monomethyl ether (0.80 mL, 5.00 mmol) and the mixture was cooled to 0°C. To this solution was added dropwise phosphorous tribromide (0.24 mL, 2.5 mmol). After the addition was complete, the reaction was allowed to stir at 0° for 10 min. To this reaction mixture was then added methanol (0.7 mL) and the reaction mixture was allowed to warm to room temperature and stir for 30 min. The reaction mixture was poured into water (1.0 mL) and the organic phase was washed with 5% sodium bicarbonate (1x) and brine (1x). The combined aqueous phase was extracted with ethyl acetate (5x) and the combined organic phases were dried over sodium sulfate. The solvent was removed *in vacuo* to afford 0.84 g (75%) of the title compound as a colorless clear liquid. FTIR (film) 2870, 1450, 1351, 1278, 1198, 1112, 1025 cm$^{-1}$. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.78 (t, J = 6.3 Hz, 2 H), 3.67-3.62 (m, 6 H), 3.54-3.52 (m, 2 H), 3.44 (t, J = 6.3 Hz, 2 H), 3.36 (s, 3 H).

*N*-[(Ethoxy ethoxy methoxy)ethyl]pyrrole (17). The procedure by Wang[4a] was modified as follows. A nitrogen purged flask equipped with a reflux condenser was charged with methylene chloride (100 mL), tetrabutylammonium bromide (37.1 g, 115 mmol), pyrrole (7.97 mL, 115 mmol) and 2-(ethoxy ethoxy methoxy)ethyl bromide (23.89 mL, 105.2 mmol) and the mixture was cooled to 0°C using an ice bath. To this solution was added dropwise 50% sodium hydroxide (100 mL). After the addition, the reaction mixture was heated to reflux and allowed to stir for 24 h. The mixture was cooled and diluted with water (50 mL) and the aqueous phase was extracted with ethyl acetate (5x). The combined organic extracts were washed with 3 N hydrochloric acid (10 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography [silica gel, ether/hexane (9:1)] to afford

15.78 g (70%) of the title compound as a yellow liquid. FTIR (film) 3099, 2873, 1500, 1450, 1348, 1282, 1195, 1108, 934, 847, 723 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.68 (t, J = 2.1 Hz, 2 H), 6.11 (t, J = 2.1 Hz, 2 H), 4.04 (t, J = 5.6 Hz, 2 H), 3.72 (t, J = 5.6 Hz, 2 H), 3.61-3.50 (m, 8 H), 3.36 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 121.19, 108.28, 72.15, 71.50, 70.85, 70.80, 70.75, 59.23, 49.66.

**N-[(Ethoxy ethoxy methoxy)ethyl]-2,5-dibromopyrrole (18).** The procedure used was analogous to Khoury's[5] method which was modified as follows. A nitrogen purged flask was charged with **17** (2.72 g, 12.7 mmol) and THF (100 mL) and the mixture was cooled to -78°C. To this solution was added N-bromosuccinimide (4.53 g, 25.5 mmol) and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 16 h, the solvent was removed *in vacuo* and the crude product was taken up in ether and filtered. The solvent was removed from the filtrate to give a residue which was purified by flash chromatography [(silica gel, ether/hexanes (6:4) to afford 4.20 g (89%) of the title compound as a yellow liquid. FTIR (film) 3120, 2873, 1646, 1515, 1450, 1420, 1370, 1282, 1115, 897, 839, 738 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.15 (s, 2 H), 4.16 (t, J = 6.6 Hz, 2 H), 3.65 (t, J = 6.6 Hz, 2 H), 3.62-3.58 (m, 6 H), 3.53-3.51 (m, 2 H), 3.36 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 112.09, 101.22, 72.08, 71.00, 70.77, 70.74, 69.47, 59.19, 46.47.

**N-[(Ethoxy ethoxy methoxy)ethyl]-2,5-dibromo-3-oxopyrrolinium-4-oxide (19).** A flask equipped with an internal thermometer was charged with **18** (1.92 g, 5.00 mmol) and the flask was cooled to 0°C by means of an ice bath. To this solution was added dropwise nitric acid (1.5 mL, 70 %) without allowing the temperature to rise above 35°C. After addition, the mixture was poured onto ice. The aqueous phase was extracted with ethyl acetate (5x) and the combined organic extracts were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chromatography [silica gel, ether/hexane (7:3)] to afford 1.61 g (78%) of the title compound as a yellow liquid. FTIR (film) 2873, 1784, 1726, 1595, 1435, 1391, 1355, 1108, 1021, 825, 730 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.79 (t, J = 5.5 Hz, 2 H), 3.64 (t, J = 5.5 Hz, 2 H), 3.61-3.56 (m, 6 H), 3.51-3.49 (m, 2 H), 3.35 (s, 3 H). $^{13}$C NMR

(100 MHz, CDCl$_3$) δ 163.91, 129.55, 72.04, 70.70, 70.69, 70.23, 67.65, 59.17, 39.10. HRMS calc'd for C$_{11}$H$_{15}$Br$_2$NO$_5$: 398.9317. Found: 398.9316.

**Poly-$N$-[(ethoxy ethoxy methoxy)ethyl]-3-oxopyrrolinium-4-oxide (20).** To a dry nitrogen purged screw-cap reaction tube charged with DME (1.5 mL) was added **19** (0.21 g, 0.50 mmol) and copper bronze (0.47 g, 7.35 mmol). The reaction tube was sealed and heated to 200°C for 48 h and then allowed to cool to 23°C. The crude product was taken up in methylene chloride and filtered. The solvent was removed from the filtrate *in vacuo* to give a residue which was dissolved in methylene chloride and fractionally precipitated by the addition of hexanes. The solid was further purified by Soxhlet extraction with hexanes for 2 d to afford 0.07 g (58%) of the title compound as a maroon solid. FTIR (film) 2888, 1697, 1435, 1399, 1108, 1014 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) δ 3.47 (br s, 9 H), 3.38 (br s, 3 H), 3.21 (br s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 169.38, 131.74, 72.94, 71.55, 71.43, 71.26, 68.36, 59.99, 39.45. $M_n$ = 8,650. $M_w/M_n$ = 1.59. Anal. calc'd for (C$_{11}$H$_{15}$NO$_5$)$_n$: C, 54.76; H, 6.26; N, 5.85. Found: C, 54.18; H, 6.25; Br<0.5; N, 5.81. $\lambda_{max}$ (CCl$_4$) = 518 nm. $\lambda_{max}$ (THF) = 496 nm. $\lambda_{max}$ (NMP) = 462, 794 nm. $\lambda_{max}$ (DMSO) = 500, 912 nm. $\lambda_{max}$ (HMPA) = 881 nm. $\lambda_{max}$ (H$_2$O) = 479, 864 nm. $\lambda_{max}$ (0.2 M NaOH) = 455, 771 nm. $\lambda_{max}$ (0.1 N HCl) = 506 nm.

**$N$-($n$-Butyl)-2,5-diphenyl-3-oxopyrrolinium-4-oxide (21).** To a dry nitrogen purged screw-cap reaction tube charged with DMF (1.5 mL) was added **8** (0.10g, 0.25 mmol), bis(dibenzylideneacetone)palladium(0) (3.6 mg, 0.006 mmol) and triphenylarsine (7.6 mg, 0.025 mmol) and the mixture was stirred for 30 min at room temperature. To this solution was added phenyltributylstannane (0.183 g, 0.50 mmol). The reaction tube was sealed and heated to 85°C for 24 h and then allowed to cool to 23°C. The crude product was poured into water and extracted with ether (3x). The combined organic extracts were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chromatography [silica gel, hexanes/ether 9:1] to afford 0.069 g (90%) of the title compound as a yellow liquid. FTIR (film) 3055, 2961, 2932, 2866, 1769, 1704, 1442, 1406, 1370, 1072, 1043, 752, 694 cm$^{-1}$. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.48 (m, 4 H), 7.34 (m, 6 H), 3.64 (t, J = 7.2 Hz, 2 H), 1.66 (p, J = 7.1

Hz, 2 H), 1.38 (sext, J = 7.8 Hz, 2 H), 0.95 (t, J = 7.3 Hz, 3 H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 171.05, 136.27, 130.13, 129.98, 128.98, 128.76, 38.40, 30.94, 20.32, 13.92. HRMS calc'd for $C_{20}H_{19}NO_2$: 305.1416. Found: 305.1403. $\lambda_{max}$ (CH$_2$Cl$_2$)= 276, 366 nm.

**Polymer 22.** To a dry nitrogen purged screw-cap reaction tube charged with toluene (1.0 mL) was added **8** (0.10g, 0.25 mmol), bis(dibenzylideneacetone)palladium(0) (14.5 mg, 0.025 mmol) and triphenylarsine (30.6 mg, 0.10 mmol) and stirred for 30 min at room temperature. To this solution was added 1,4-bis(tri-*n*-butylstannyl)benzene (0.164 g, 0.250 mmol). The reaction tube was sealed and heated to 120°C for 48 h and then allowed to cool to 23°C. The crude product was poured into water and extracted with methylene chloride (3x). The combined organic extracts were dried over sodium sulfate and the solvent was removed *in vacuo* to give a residue which was dissolved in methylene chloride and fractionally precipitated by the addition of methanol. The solid was further purified by Soxhlet extraction with hexanes for 3 d to afford 51.3 mg (89%) of the title compound as an orange viscous liquid. FTIR (film) 2961, 2932, 2873, 1762, 1704, 1442, 1399, 1362, 1181, 1108, 1050, 926, 832, 752 cm$^{-1}$. $^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.6 - 7.3 (m, 2.4 H), 3.60 (m, 2 H), 1.60 (br s, 2 H), 1.33 (br s, 2.5 H), 0.92 (br s, 3.2 H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.92, 136.48, 130.86, 39.10, 30.47, 20.81, 14.39. $M_n$ = 2,010. $M_w/M_n$ = 1.24. Anal. calc'd for $(C_{14}H_{13}NO_2)n$: C, 73.99; H, 5.76; N, 6.16. Found: C, 74.64,; H, 8.05; N, 3.99 (C and H content are high and N content is low due to significant terminal SnBu$_3$ end groups present in this low molecular weight material as seen by NMR). $\lambda_{max}$ (THF) = 410 nm.

**Supplementary Material Available:** Spectroscopic plots are available for all the monomers and polymers. This material is contained in many libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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